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TWO-PHOTON LASER SPECTROSCOPY OF TRANSITION IONS IN CRYSTALS : INTER-CONFIGURATIONAL TRANSITIONS

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ABSTRACT

Symmetry adaptation techniques are applied to the determination of the intensity of two-photon absorption transitions, between Stark levels of configurations with opposite parities, for transition ions in finite symmetry environments. The equivalence between third-order mechanisms and second- plus first-order mechanisms is clearly established. A compact formula is derived for the intensity of a two-photon transition between two levels with well-defined symmetries. A set of (selection) rules which controls the number of intensity parameters for inter-configurational transitions is given. The formalism is illustrated with the case of an ion with $4f$ configuration in tetragonal symmetry.

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Symmetry adaptation techniques are applied to the determination of the intensity of two-photon absorption transitions, between Stark levels of configurations with opposite parities, for transition ions in finite symmetry environments. The equivalence between third order mechanisms and second-plus first-order mechanisms is clearly established. A compact formula is derived for the intensity of a two-photon transition between two levels with well-defined symmetries. A set of (selection) rules which controls the intensity parameters for inter-configurational transitions is given. The formalism is illustrated with the case of an ion with $4f$ configuration in tetragonal symmetry.

1. Introduction

The theory of two-photon absorption spectroscopy for an ion with a partly-filled shell embedded in a crystal has received a great deal of attention in recent years [1-13]. It is the aim of this paper to develop a formalism for $n\ell \rightarrow n'\ell'$ inter-configurational two-photon transitions when the two involved (one-electron) configurations have opposite parities. This problem has been already addressed by Gayen and Hamilton [7], Gayen *et al.* [7], Leavitt [11], Makhanek *et al.* [4], and Sztucki and Strȩk [9]. However, little attention has been paid to symmetry adaptation techniques (i.e., group-theoretical considerations from both a qualitative and a quantitative viewpoint) for inter-configurational two-photon transitions. In this paper, we follow the general line adopted in Refs. [12,13] for intra-configurational two-photon transitions in order to develop a model incorporating parity violation by the odd components of the crystal-field interaction and symmetry adaptation to the chain $O(3)^* \supset G^*$. (The group G^* denotes the double group of the point symmetry group G of the ion site.) The model is applied to the case of the Ce^{3+} ion in CaF_2 [7] and $LuPO_4$ [14].

2. Transition element

We begin with the (electronic) transition matrix element $M_{i\rightarrow f}$ for a two-photon absorption between an initial state i and a final state f. We work in the framework of the electric dipolar approximation and use single-mode excitations of energy $\hbar\omega$, wave-vector $\vec{k}$, and polarization vector $\vec{\mathcal{E}}$ for the radiation field. (For the sake of simplicity, we first consider that the two absorbed photons are identical.) Then, the matrix element $M_{i\rightarrow f}$ is

given by [15,16]

$$M_{i\to f} = \sum_v \frac{1}{\Delta_v} \left(f|\vec{D}.\vec{\mathcal{E}}|v \right) \left(v|\vec{D}.\vec{\mathcal{E}}|i \right) \qquad \Delta_v = E_i - (E_v - \hbar\omega) \tag{1}$$

with evident notations. For linear polarization, the spherical components of $\vec{\mathcal{E}}$ are

$$\mathcal{E}_0 = \cos\theta \qquad \mathcal{E}_{\pm 1} = \mp \frac{1}{\sqrt{2}} \, \sin\theta \, \exp(\pm i\varphi) \tag{2}$$

where (θ, φ) are the polar angles of the unit polarization vector $\vec{\mathcal{E}}$ with respect to the crystallographic c-axis. For circular polarization, the components $\mathcal{E}_q$ $(q = -1, 0, +1)$ of $\vec{\mathcal{E}}$ are given by

$$\mathcal{E}_{-q} = -\delta(q, +1) \quad \text{or} \quad \mathcal{E}_{-q} = -\delta(q, -1) \tag{3}$$

for right or left circular polarization, respectively, when the wave vector $\vec{k}$ is parallel to the c-axis.

The state vectors corresponding to i and f may be (partially) labelled by the irreducible representation classes of the group G^*. We thus have

$$|i) \equiv |n\ell i \Gamma\gamma) \qquad |f) \equiv |n'\ell' f \Gamma'\gamma') \tag{4}$$

where the labels γ or γ' may serve as multiplicity labels when the dimensions of the irreducible representation classes Γ or Γ' are greater than 1, respectively. The state vectors (4) can be expanded in terms of symmetry adapted state vectors as

$$\begin{aligned} |n\ell i\Gamma\gamma) &= \sum_{ja} \; |ns\ell ja\Gamma\gamma) \; c(n\ell ja\Gamma; i) \\ |n'\ell' f\Gamma'\gamma') &= \sum_{j'a'} \; |n's\ell' j'a'\Gamma'\gamma') \; c(n'\ell' j'a'\Gamma'; f) \end{aligned} \tag{5}$$

with

$$\begin{aligned} |ns\ell ja\Gamma\gamma) \; &= \; \sum_m \; |ns\ell jm) \; (jm|ja\Gamma\gamma) \\ |n's\ell' j'a'\Gamma'\gamma') \; &= \; \sum_{m'} \; |n's\ell' j'm') \; (j'm'|j'a'\Gamma'\gamma') \end{aligned} \tag{6}$$

where the expansion coefficients of type $(JM|Ja\Gamma\gamma)$ in (6) are reduction coefficients to pass from the $\{JM\}$ scheme to the $\{Ja\Gamma\gamma\}$ scheme [17]. The coefficients c in (5) are obtainable from the diagonalization-optimization of the Hamiltonian H describing the ion in its environment. (In (5) and (6), s stands for 1/2.)

The transition matrix element $M_{i\to f}$ given by (1) and (4)-(6) vanishes since the initial and final states have opposite parities. In order to generate non-vanishing transition matrix elements, we must admit that the parity of the initial and final state vectors is not well-defined. This is the case if the crystal-field part of H contains odd components either because the site symmetry is non-centrosymmetric or because of the vibration of

the ligands. Therefore, we have to replace the initial and final state vectors, respectively, by

$$|i> = |i) - \frac{1}{\Delta} \sum_{x'} |n'\ell' x' \Gamma\gamma)(n'\ell' x' \Gamma\gamma|O|n\ell i \Gamma\gamma) \tag{7}$$

and

$$|f> = |f) + \frac{1}{\Delta} \sum_{x} |n\ell x \Gamma'\gamma')(n\ell x \Gamma'\gamma'|O|n'\ell' f \Gamma'\gamma') \tag{8}$$

In deriving (7) and (8), we have made use of the following points.

(i) We have supposed that the scrambling between the state vectors of opposite parities is restriced to the interaction, via the operator O, of the configurations $n\ell$ and $n'\ell'$. The operator O can be viewed as the odd part of the crystal-field interaction contained in H and thus can be developed either as

$$O = \sum_k \sum_q B[kq]\, C^k_q \tag{9a}$$

in terms of standard components C^k_q or as

$$O = \sum_k \sum_{a_0} B[ka_0]\, C^k_{a_0\Gamma_0\gamma_0} \tag{9b}$$

in terms of G-invariant components $C^k_{a_0\Gamma_0\gamma_0}$. (The label Γ_0 stands for the identity representation class of the group G.) The one-electron tensor operator C^k in (9), with *spherical components* C^k_q (adapted to the chain $O(3) \supset O(2)$) or *symmetry adapted components* $C^k_{a_0\Gamma_0\gamma_0}$ (adapted to the chain $O(3) \supset G$), is defined through

$$(\ell' \| C^k \| \ell) = (-)^{\ell'} [(2\ell'+1)(2\ell+1)]^{\frac{1}{2}} \begin{pmatrix} \ell' & k & \ell \\ 0 & 0 & 0 \end{pmatrix} \tag{10}$$

(The crystal-field parameters $B[kq]$ in (9a) correspond to the Rajnak-Wybourne parameters in a somewhat different form since we want to reserve the notation B^k_q for the q-th component of a tensor B^k to be defined below.)

(ii) Furthermore, we have taken into account that, due to the G-invariance of the operator O, the quantum numbers $\Gamma\gamma$ and $\Gamma'\gamma'$ remain good quantum numbers for the states i and f, respectively.

(iii) Finally, we have applied the (quasi-closure) approximation (cf. Refs. [18,19])

$$\begin{aligned} E(n'\ell' x' \Gamma\gamma) - E(n\ell i \Gamma\gamma) &= E_{n'\ell'} - E_{n\ell} \equiv +\Delta \\ E(n\ell x \Gamma'\gamma') - E(n'\ell' f \Gamma'\gamma') &= E_{n\ell} - E_{n'\ell'} \equiv -\Delta \end{aligned} \tag{11}$$

where $\Delta = 2\hbar\omega$, a function of the common energy $\hbar\omega$ of the two identical photons.

The next approximation is to suppose that the intermediate states v in (1) are mixed by the operator O in a way similar to the one for the states i and f and that, in addition, they may have a predominant character of type $n\ell$ or $n'\ell'$. Consequently, we take

$$|v> = |n\ell x_v \Gamma_v \gamma_v) - \frac{1}{\Delta} \sum_{x_v'} |n'\ell' x_v' \Gamma_v \gamma_v)(n'\ell' x_v' \Gamma_v \gamma_v | O | n\ell x_v \Gamma_v \gamma_v) \tag{12}$$

or

$$|v> = |n'\ell' x_v \Gamma_v \gamma_v) + \frac{1}{\Delta} \sum_{x_v'} |n\ell x_v' \Gamma_v \gamma_v)(n\ell x_v' \Gamma_v \gamma_v | O | n'\ell' x_v \Gamma_v \gamma_v) \tag{13}$$

according to whether as the state v has an $n\ell$ or $n'\ell'$ predominant character.

The transition matrix element (1) now can be non-zero if we replace the initial, intermediate and final state vectors by the corresponding mixed state vectors. As a result, we obtain

$$\begin{aligned} -\frac{1}{2}\,\Delta^2\, M(2+1)_{i\to f} = & \\ & \sum_{x x_v \Gamma_v \gamma_v} (f|O|n\ell x \Gamma' \gamma')(n\ell x \Gamma' \gamma' | \vec{D}.\vec{\mathcal{E}} | n'\ell' x_v \Gamma_v \gamma_v)(n'\ell' x_v \Gamma_v \gamma_v | \vec{D}.\vec{\mathcal{E}} | i) \\ +2 & \sum_{x_v' x_v \Gamma_v \gamma_v} (f|\vec{D}.\vec{\mathcal{E}}|n\ell x_v \Gamma_v \gamma_v)(n\ell x_v \Gamma_v \gamma_v | O | n'\ell' x_v' \Gamma_v \gamma_v)(n'\ell' x_v' \Gamma_v \gamma_v | \vec{D}.\vec{\mathcal{E}} | i) \\ + & \sum_{x' x_v \Gamma_v \gamma_v} (f|\vec{D}.\vec{\mathcal{E}}|n\ell x_v \Gamma_v \gamma_v)(n\ell x_v \Gamma_v \gamma_v | \vec{D}.\vec{\mathcal{E}} | n'\ell' x' \Gamma \gamma)(n'\ell' x' \Gamma \gamma | O | i) \end{aligned} \tag{14}$$

where we have neglected the terms in $(1/\Delta)^4$ in $M_{i\to f}$ and taken into consideration the hermiticity property of the operator O. The notation $M(2+1)_{i\to f}$ for $M_{i\to f}$ indicates that the transition matrix element has been calculated from second-order time-dependent perturbation theory and first-order time-independent perturbation theory.

It is interesting to note that the result (14) can be obtained in a different way by invoking third-order mechanisms and by making use of approximations similar to the ones employed for deriving $M(2+1)_{i\to f}$. By third-order mechanisms, we mean that we start from the transition moment for a three-photon absorption transition where we replace one of the operators $\vec{D}.\vec{\mathcal{E}}$ by the operator O with change of denominators and appropriate permutations. This leads to

$$\begin{aligned} M(3)_{i\to f} = & \sum_{v_1 v_2} \frac{1}{\Delta_{12}} (f|O|v_1)(v_1|\vec{D}.\vec{\mathcal{E}}|v_2)(v_2|\vec{D}.\vec{\mathcal{E}}|i) \\ & + \sum_{v_1 v_2} \frac{1}{\Delta_{12}} (f|\vec{D}.\vec{\mathcal{E}}|v_1)(v_1|O|v_2)(v_2|\vec{D}.\vec{\mathcal{E}}|i) \\ & + \sum_{v_1 v_2} \frac{1}{\Delta_{12}} (f|\vec{D}.\vec{\mathcal{E}}|v_1)(v_1|\vec{D}.\vec{\mathcal{E}}|v_2)(v_2|O|i) \end{aligned} \tag{15}$$

The notation $M(3)_{i\to f}$ for $M_{i\to f}$ is a reminder that the calculation of the transition matrix element arises from third-order time-dependent perturbation theory. The state vectors in

(15) are non-mixed state vectors. Furthermore, we assume in (15) that the intermediate states v are of either $n\ell$ or $n'\ell'$ type. By using the approximation (11), we get

$$\Delta_{12}(\text{1st sum}) = -\frac{1}{2}\Delta^2 \qquad \Delta_{12}(\text{2nd sum}) = -\frac{1}{4}\Delta^2 \qquad \Delta_{12}(\text{3rd sum}) = -\frac{1}{2}\Delta^2 \tag{16}$$

so that we finally arrive at the important result

$$M(3)_{i\to f} = M(2+1)_{i\to f} \tag{17}$$

At this stage, it should be noted that the equivalence described by (17) also holds when the two absorbed photons are not identical. In this case, we have to replace Δ by $\hbar\omega_1 + \hbar\omega_2$ (for more details, see the thesis by one of the authors (M. D.)).

3. Intensities

Equation (14) and its analogue in terms of non-identical photons can be worked out by using recoupling and symmetry adaptation techniques. In the case of two non-identical photons, this leads to

$$M_{i\to f} = (n'\ell' f\Gamma'\gamma'|H_{eff}|n\ell i\Gamma\gamma) \tag{18}$$

where the effective transition operator H_{eff} reads

$$H_{eff} = \sum_{hkt} M[(hk)t]\left(\{\{\mathcal{E}_1\mathcal{E}_2\}^h B^k\}^t \,.\, U^t\right) \tag{19}$$

In eq. (19), $\{\mathcal{E}_1\mathcal{E}_2\}^h$ is the tensor product of the polarization vectors $\vec{\mathcal{E}}_1$ and $\vec{\mathcal{E}}_2$ for the two photons with $h = 0, 1, 2$. (When $\vec{\mathcal{E}}_1 = \vec{\mathcal{E}}_2$, we have only $h = 0, 2$.) Furthermore, the tensor B^k in (19) has its spherical components B^k_q given by

$$B^k_q = (-)^q\, B[k, -q] \tag{20}$$

where the parameters $B[kq]$ are the expansion coefficients of the crystal-field interaction O (see eq. (9a)). Hence, k may take the values $|\ell - \ell'|$, $|\ell - \ell'| + 2$, ..., $\ell + \ell'$. Finally, the (one-electron) tensor operator $U^t \equiv u^t$ in (19) is such that

$$(\ell\|u^t\|\ell') = 1 \tag{21}$$

and its rank t is restricted by the fact that (ℓ, ℓ', t), (j, j', t), and (h, k, t) should form three triads.

The parameters $M[(hk)t]$ occurring in (19) can be written as

$$M[(hk)t] = \frac{1}{\Delta}\,[(2t+1)(2h+1)]^{\frac{1}{2}}\, e^2\, (n\ell|r|n'\ell')^2\, (\ell\|C^1\|\ell')^2\, (\ell\|C^k\|\ell')$$
$$\left[x \begin{Bmatrix} h & k & t \\ 1 & \ell & \ell' \\ 1 & \ell' & \ell \end{Bmatrix} + y \begin{Bmatrix} h & k & t \\ \ell' & \ell & \ell \end{Bmatrix} \begin{Bmatrix} 1 & 1 & h \\ \ell & \ell & \ell' \end{Bmatrix} + z \begin{Bmatrix} h & k & t \\ \ell & \ell' & \ell' \end{Bmatrix} \begin{Bmatrix} 1 & 1 & h \\ \ell' & \ell' & \ell \end{Bmatrix}\right] \tag{22}$$

where Δ stands here for $\hbar\omega_1 + \hbar\omega_2 = E_{n'\ell'} - E_{n\ell}$ and the factors x, y, and z are

$$x = (-)^t \left[1 + (-)^h\right] \left[\frac{1}{\hbar\omega_1} + \frac{1}{\hbar\omega_2}\right] \qquad y = (-)^t \left[\frac{1}{\hbar\omega_1} + (-)^h \frac{1}{\hbar\omega_2}\right] \qquad z = (-)^{t+1}\, y \quad (23)$$

It is to be mentioned that, in the special case where the photons 1 and 2 are identical, the expressions for $M[(hk)t]$ and H_{eff} agree with those derived by Leavitt [11] from second quantization techniques and by Sztucki and Stręk [9] from ordinary Wigner-Racah calculus. (The results of Leavitt and of Sztucki and Stręk are derived in a spherical basis rather than in a basis adapted to the chain $O(3)^* \supset G^*$.)

By making use of symmetry adaptation techniques for the chain $O(3)^* \supset G^*$, it can be shown, from eqs. (5), (18) and (19), that

$$\begin{aligned} M_{i\to f} = -\sum_{j'a'} \sum_{ja} \sum_{hkt} \sum_{a''} \sum_{\Gamma''} \sum_{\gamma''} \sum_{\bar{a}''} \sum_{a_0} & c(j'a'\Gamma'; f)^*\, c(ja\Gamma; i) \\ & (2t+1)^{\frac{1}{2}}\, (s\ell j \| u^t \| s\ell' j')\, M[(hk)t]\, B[ka_0]^*\, \{\mathcal{E}_1\mathcal{E}_2\}^h_{\bar{a}''\Gamma''\gamma''} \\ & f \begin{pmatrix} t & h & k \\ a''\Gamma''\gamma'' & \bar{a}''\Gamma''\gamma'' & a_0\Gamma_0\gamma_0 \end{pmatrix}^* f \begin{pmatrix} j & j' & t \\ a\Gamma\gamma & a'\Gamma'\gamma' & a''\Gamma''\gamma'' \end{pmatrix}^* \end{aligned} \quad (24)$$

where the f coupling coefficients are defined by means of the generic formula [17]

$$\begin{aligned} f \begin{pmatrix} j_1 & j_2 & k \\ \mu_1 & \mu_2 & \mu \end{pmatrix} = \sum_{m_1 q m_2} & (-)^{j_1 - m_1} \begin{pmatrix} j_1 & k & j_2 \\ -m_1 & q & m_2 \end{pmatrix} \\ & (j_1 m_1 | j_1 \mu_1)^*\, (kq|k\mu)\, (j_2 m_2 | j_2 \mu_2) \end{aligned} \quad (25)$$

with the abbreviations $\mu_i \equiv a_i\Gamma_i\gamma_i$ $(i = 1, 2)$ and $\mu \equiv a\Gamma\gamma$. (Note that the f coefficient is simply a symmetry adapted version of the coupling factor which occurs, besides the reduced matrix element, in the ordinary Wigner-Eckart theorem.) In order to obtain eq. (24), we have used a property of the f coefficients which arises when $\mu \equiv a_0\Gamma_0\gamma_0$ (see Ref. [17]).

The next step is to calculate the intensity strength

$$S_{\Gamma\to\Gamma'} \equiv S_{i(\Gamma)\to f(\Gamma')} = \sum_{\gamma\gamma'} \left| M_{i(\Gamma\gamma)\to f(\Gamma'\gamma')} \right|^2 \quad (26)$$

where the sum on γ and γ' must be extended over all the Stark components of the initial and final states (of symmetry Γ and Γ'), respectively. The calculation of $S_{\Gamma\to\Gamma'}$ can be achieved by using : (i) eq. (24) twice, (ii) the factorization lemma for the f coefficients [17], and (iii) the orthonormality-completeness property for the f coefficients [17]. As a net result, we get the compact formula

$$S_{\Gamma\to\Gamma'} = \sum_{h,\bar{h}} \sum_{r,\bar{r}} \sum_{\Gamma''} I[h\bar{h}r\bar{r}\Gamma''; \Gamma\Gamma'] \sum_{\gamma''} \{\mathcal{E}_1\, \mathcal{E}_2\}^h_{r\Gamma''\gamma''} \left(\{\mathcal{E}_1\, \mathcal{E}_2\}^{\bar{h}}_{\bar{r}\Gamma''\gamma''}\right)^* \quad (27)$$

The intensity parameters I in eq. (27) may be developed as

$$I[h\bar{h}r\bar{r}\Gamma'';\Gamma\Gamma'] = [\Gamma'']^{-1}\,[\Gamma]\sum_{j'a'}\sum_{ja}\sum_{\bar{j}'\bar{a}'}\sum_{\bar{j}\bar{a}}\sum_{tp}\sum_{\bar{t}\bar{p}} Z_h(j'a'\Gamma', ja\Gamma, hr\Gamma'', tp\Gamma'')\, Z_{\bar{h}}(\bar{j}'\bar{a}'\Gamma', \bar{j}\bar{a}\Gamma, \bar{h}\bar{r}\Gamma'', \bar{t}\bar{p}\Gamma'')^* \sum_{\beta}(j'a'\Gamma' + tp\Gamma''|ja\beta\Gamma)\,(\bar{j}'\bar{a}'\Gamma' + \bar{t}\bar{p}\Gamma''|\bar{j}\bar{a}\beta\Gamma)^* \tag{28}$$

where the coefficient

$$Z_h(j'a'\Gamma', ja\Gamma, hr\Gamma'', tp\Gamma'') = (2j+1)^{-\frac{1}{2}}\,(2t+1)^{\frac{1}{2}}\,c(j'a'\Gamma';f)^*\,c(ja\Gamma;i)\,(s\ell j\|u^t\|s\ell' j') \sum_{k}\sum_{a_0} M[(hk)t]\,B[ka_0]^*\,f\begin{pmatrix} t & h & k \\ p\Gamma''\gamma'' & r\Gamma''\gamma'' & a_0\Gamma_0\gamma_0 \end{pmatrix}^* \tag{29}$$

turns out to be independent of the label γ''. The coefficients $(\ +\ |\ )$ in (28) are isoscalar factors for the reduction $O(3)^* \to G^*$ [17].

The intensity formula (27) has the same form as the one obtained in a previous work [12] for intra-configurational two-photon transitions. The intensity parameters I in (27) exhibit the symmetry property

$$I[h\bar{h}r\bar{r}\Gamma'';\Gamma\Gamma'] = I[\bar{h}h\bar{r}r\Gamma'';\Gamma\Gamma']^* \tag{30}$$

which corresponds to the real character of $S_{\Gamma\to\Gamma'}$. Furthermore, they can be factorized into two similar factors when the group G^* is multiplicity-free since the sum over β in (28) disappears in this case.

The number of *a priori* independent intensity parameters I in (27) is controlled by the property (30) and the following selection rules.

Rule 1. In most cases, there is no summation in (27) over the multiplicity labels r and $\bar{r}$.

Rule 2. The summation in (27) over Γ'' is restricted by the group-theoretical rules

$$\Gamma'' \subset (h) \qquad \Gamma'' \subset (\bar{h}) \qquad \Gamma'' \subset \Gamma \otimes \Gamma'^* \tag{31}$$

where (h) and $(\bar{h})$ are irreducible representation classes of $O(3)$. Similarly, we must have $\Gamma'' \subset (t)$ and $\Gamma'' \subset (\bar{t})$ in (28) and (29).

Rule 3. In the cases where either $\vec{\mathcal{E}}_1 = \vec{\mathcal{E}}_2$ or $\hbar\omega_1 = \hbar\omega_2$, the summation in (27) over h and $\bar{h}$ is restricted to the values $0, 2$ but h and $\bar{h}$ can take the values $0, 1, 2$ when, simultaneously, $\vec{\mathcal{E}}_1 \neq \vec{\mathcal{E}}_2$ and $\hbar\omega_1 \neq \hbar\omega_2$.

4. Illustration

We now illustrate the model developed in the present paper with the case of a $4f \to 5d$ transition for an ion of configuration $4f^1$ in tetragonal symmetry with $G = C_{4v}$ or D_{2d}. In this case, there are four possible transitions since Γ and Γ' may be equal to Γ_6 or Γ_7. We consider only the situation where the two photons are identical. Then, the possible values of h and $\bar{h}$ in (27) are 0,2 and there is no summation on r and $\bar{r}$ in (27). In addition, the

irreducible representation classes Γ'' in (27) are $\Gamma'' = A_1, E$ for the transitions $\Gamma_6 \to \Gamma_6$ or $\Gamma_7 \to \Gamma_7$ and $\Gamma'' = B_1, B_2, E$ for the transitions $\Gamma_6 \to \Gamma_7$ or $\Gamma_7 \to \Gamma_6$. By developing (27), we get

$$\begin{aligned} S_{\Gamma\to\Gamma} =& I[02A_1;\Gamma\Gamma]\,\{\mathcal{E}\mathcal{E}\}^0_{A_1}\,(\{\mathcal{E}\mathcal{E}\}^2_{A_1})^* + I[20A_1;\Gamma\Gamma]\,(\{\mathcal{E}\mathcal{E}\}^0_{A_1})^*\,\{\mathcal{E}\mathcal{E}\}^2_{A_1} + \\ & I[00A_1;\Gamma\Gamma]\,|\{\mathcal{E}\mathcal{E}\}^0_{A_1}|^2 + I[22A_1;\Gamma\Gamma]\,|\{\mathcal{E}\mathcal{E}\}^2_{A_1}|^2 + I[22E;\Gamma\Gamma]\sum_{\gamma''}|\{\mathcal{E}\mathcal{E}\}^2_{E\gamma''}|^2 \end{aligned} \tag{32}$$

for $\Gamma = \Gamma' = \Gamma_6$ or Γ_7 and

$$S_{\Gamma\to\Gamma'} = I[22B_1;\Gamma\Gamma']|\{\mathcal{E}\mathcal{E}\}^2_{B_1}|^2 + I[22B_2;\Gamma\Gamma']|\{\mathcal{E}\mathcal{E}\}^2_{B_2}|^2 + I[22E;\Gamma\Gamma']\sum_{\gamma''}|\{\mathcal{E}\mathcal{E}\}^2_{E\gamma''}|^2 \tag{33}$$

for $\Gamma \neq \Gamma' = \Gamma_6$ or Γ_7. The polarization factors in (32) and (33) can be calculated in an $O(3) \supset C_{\infty v} \supset C_{4v} \supset C_{2v}$ basis to be

$$\begin{aligned} \{\mathcal{E}\mathcal{E}\}^0_{A_1} &= \frac{-1}{\sqrt{3}} \quad \text{or} \quad 0 \\ \{\mathcal{E}\mathcal{E}\}^2_{A_1} &= \frac{1}{\sqrt{6}}(3\cos^2\theta - 1) \quad \text{or} \quad 0 \\ \{\mathcal{E}\mathcal{E}\}^2_{B_1} &= \frac{1}{\sqrt{2}}\sin^2\theta\cos 2\varphi \quad \text{or} \quad +\frac{1}{\sqrt{2}} \\ \{\mathcal{E}\mathcal{E}\}^2_{B_2} &= \frac{i}{\sqrt{2}}\sin^2\theta\sin 2\varphi \quad \text{or} \quad \pm\frac{1}{\sqrt{2}} \\ \sum_{\gamma''}|\{\mathcal{E}\mathcal{E}\}^2_{E\gamma''}|^2 &= \frac{1}{2}\sin^2 2\theta \quad \text{or} \quad 0 \end{aligned} \tag{34}$$

according to as the polarization is linear or circular, respectively. In the detail, equations (32) and (33) lead to (for linear polarization)

$$\begin{aligned} S_{\Gamma_6\to\Gamma_6} &= a + b\,\pi_1 + c\,\pi_1^2 + d\,\pi_2 \\ S_{\Gamma_7\to\Gamma_7} &= a' + b'\,\pi_1 + c'\,\pi_1^2 + d'\,\pi_2 \\ S_{\Gamma_6\to\Gamma_7} &= f\,\pi_2 + h\,\pi_4 + i\,\pi_5 \\ S_{\Gamma_7\to\Gamma_6} &= f'\,\pi_2 + h'\,\pi_4 + i'\,\pi_5 \end{aligned} \tag{35}$$

where the angular functions π_i $(i = 1, 2, 4, 5)$ are defined by

$$\pi_1 = 3\,\cos^2\theta\,-\,1 \qquad \pi_2 = \sin^2 2\theta \qquad \pi_4 = \sin^4\theta\,\cos^2 2\varphi \qquad \pi_5 = \sin^4\theta\,\sin^2 2\varphi \tag{36}$$

and the various parameters $a, \cdots, i$ and $a', \cdots, i'$ read

$$\begin{aligned}
a &= (1/3)\, I[00A_1;\Gamma_6\Gamma_6] & a' &= (1/3)\, I[00A_1;\Gamma_7\Gamma_7] \\
b &= -(\sqrt{2}/3)\, \mathrm{Re}[I[02A_1;\Gamma_6\Gamma_6]] & b' &= -(\sqrt{2}/3)\, \mathrm{Re}[I[02A_1;\Gamma_7\Gamma_7]] \\
c &= (1/6)\, I[22A_1;\Gamma_6\Gamma_6] & c' &= (1/6)\, I[22A_1;\Gamma_7\Gamma_7] \\
d &= (1/2)\, I[22E;\Gamma_6\Gamma_6] & d' &= (1/2)\, I[22E;\Gamma_7\Gamma_7] \\
f &= (1/2)\, I[22E;\Gamma_6\Gamma_7] & f' &= (1/2)\, I[22E;\Gamma_7\Gamma_6] \\
h &= (1/2)\, I[22B_1;\Gamma_6\Gamma_7] & h' &= (1/2)\, I[22B_1;\Gamma_7\Gamma_6] \\
i &= (1/2)\, I[22B_2;\Gamma_6\Gamma_7] & i' &= (1/2)\, I[22B_2;\Gamma_7\Gamma_6]
\end{aligned} \tag{37}$$

in terms of the intensity parameters I. The latter parameters are calculable from (28) and (29) together with (22). (Equation (28) shows that the parameters I can be expressed here as the product of two similar factors since there is no internal multiplicity label β for tetragonal symmetry.)

4.1. Ce^{3+} in CaF_2

Two-photon experiments for the ion Ce^{3+} (of configuration $4f^1$) in CaF_2 (with local site symmetry $G = C_{4v}$) have been reported in Ref. [7]. The polarization dependence of the inter-configurational transition ${}^2F_{5/2}(\Gamma_7) \rightarrow 5d(\Gamma_7)$ (between the ground state of the $4f^1$ configuration and the ground state of the $5d^1$ configuration) has been interpreted by Gayen and Hamilton [7] on the basis of the group-theoretical formalism from Bader and Gold [3] and by Makhanek *et al.* [4] on a more quantitative basis.

From equations (35) and (36), the intensity of the ${}^2F_{5/2}(\Gamma_7) \rightarrow 5d(\Gamma_7)$ transition can be rewritten as

$$S_{\Gamma_7\rightarrow\Gamma_7} = A + B\sin^2\theta + C\sin^2 2\theta \tag{38}$$

with

$$\begin{aligned}
A &= (1/3)\, I[00A_1;\Gamma_7\Gamma_7] + (2/3)\, I[22A_1;\Gamma_7\Gamma_7] - 2(\sqrt{2}/3)\, \mathrm{Re}[I[02A_1;\Gamma_7\Gamma_7]] \\
B &= -(1/2)\, I[22A_1;\Gamma_7\Gamma_7] + \sqrt{2}\, \mathrm{Re}[I[02A_1;\Gamma_7\Gamma_7]] \\
C &= -(3/8)\, I[22A_1;\Gamma_7\Gamma_7] + (1/2)\, I[22E;\Gamma_7\Gamma_7]]
\end{aligned} \tag{39}$$

The F^- charge compensator in CaF_2 has an equal probability of going into an interstitial site along the [100], [010] or [001] directions. Therefore, the intensity strength of the ${}^2F_{5/2}(\Gamma_7) \rightarrow 5d(\Gamma_7)$ transition has to be averaged as

$$S_{\Gamma_7\rightarrow\Gamma_7} = \frac{1}{3}\left(S([100])_{\Gamma_7\rightarrow\Gamma_7} + S([010])_{\Gamma_7\rightarrow\Gamma_7} + S([001])_{\Gamma_7\rightarrow\Gamma_7}\right) \tag{40}$$

Equations (38) and (40) yield

$$\begin{aligned}
S_{\Gamma_7\rightarrow\Gamma_7} &= A + (2/3)B + (2/3)C\sin^2 2\theta \\
S_{\Gamma_7\rightarrow\Gamma_7} &= A + (1/3)B + (2/3)C + (1/3)B\sin^2\theta - (1/3)C\sin^2 2\theta \\
S_{\Gamma_7\rightarrow\Gamma_7} &= A + (2/3)B + (2/3)C
\end{aligned} \tag{41}$$

for ($\vec{k}\|[100]$ $\vec{\mathcal{E}}\|[010]$), ($\vec{k}\|[110]$ $\vec{\mathcal{E}}\|[001]$), and ($\vec{k}\|[111]$ $\vec{\mathcal{E}}\|[1\bar{1}0]$), respectively, which correspond to the three experimental situations considered by Gayen and Hamilton [7]. The intensity formulas (41) formally exhibit the same θ-dependence than those obtained in Ref. [7]. Equations (41), where the intensity parameters A, B and C can be *a priori* calculated from the formalism developed in section 3, constitutes a justification of the purely group-theoretical approach used in Ref. [7]. (Let us remember that the approach used in Ref. [7] is based on group-theoretical selection rules for intra-configurational transitions.) Finally, it should be noted that the scalar terms (corresponding to h or $\bar{h} = 0$ in (27)), described in (41) by the intensity parameters $I[00A_1;\Gamma_7\Gamma_7]$ and $I[02A_1;\Gamma_7\Gamma_7]$, do not occur in the treatment of Ref. [4].

4.2. Ce^{3+} in $LuPO_4$

Inter-configurational two-photon transitions for Ce^{3+} in $LuPO_4$ (site symmetry $G = D_{2d}$) have been observed by Piehler [14]. The transitions investigated are of the type ${}^2F_{5/2}(\Gamma_6) \rightarrow 5d$ (between the ground state of the $4f^1$ configuration and the Stark components of the $5d^1$ configuration) with linear polarization. Piehler has obtained a first transition (at $2\hbar\omega = 30460$ cm^{-1}) whose intensity vanishes when the two (identical) photons are polarized along the z-axis and a second one (at $2\hbar\omega \approx 40000$ cm^{-1}) whose intensity does not vanish for polarization along the z-axis.

The symmetry species of the $5d$ final states reached in Ref. [14] can be easily determined from (35) and (36). Indeed, from (35) and (36), the intensities of the transitions ${}^2F_{5/2}(\Gamma_6) \rightarrow 5d(\Gamma_6$ or $\Gamma_7)$ can be seen to be

$$\begin{aligned} S_{\Gamma_6\rightarrow\Gamma_6} &= A' + B'\sin^2\theta + C'\sin^2 2\theta \\ S_{\Gamma_6\rightarrow\Gamma_7} &= A''\sin^4\theta\cos^2 2\varphi + B''\sin^4\theta\sin^2 2\varphi + C''\sin^2 2\theta \end{aligned} \tag{42}$$

where

$$\begin{aligned} A' &= (1/3)\,I[00A_1;\Gamma_6\Gamma_6] + (2/3)\,I[22A_1;\Gamma_6\Gamma_6] - 2(\sqrt{2}/3)\,\mathrm{Re}[I[02A_1;\Gamma_6\Gamma_6]] \\ B' &= -(1/2)\,I[22A_1;\Gamma_6\Gamma_6] + \sqrt{2}\,\mathrm{Re}[I[02A_1;\Gamma_6\Gamma_6]] \\ C' &= -(3/8)\,I[22A_1;\Gamma_6\Gamma_6] + (1/2)\,I[22E;\Gamma_6\Gamma_6]] \\ A'' &= (1/2)\,I[22B_1;\Gamma_6\Gamma_7] \quad B'' = (1/2)\,I[22B_2;\Gamma_6\Gamma_7] \quad C'' = (1/2)\,I[22E;\Gamma_6\Gamma_7] \end{aligned} \tag{43}$$

Thus, equation (42) shows that only the intensity strength $S_{\Gamma_6\rightarrow\Gamma_7}$ vanishes when the electric field is polarized along the z-axis (i.e., $\theta = 0$). As a consequence, the symmetry of the final states is Γ_7 for the first transition (at 30460 cm^{-1}) and Γ_6 for the second transition (at 40000 cm^{-1}). This result is in accordance with the one obtained by Piehler [14] on the basis of selection rules derived from (qualitative) group-theoretical considerations. Here again, it is to be mentioned that the intensities (42) are calculable from *ab initio* principles once the intensity parameters (43) are known.

5. Concluding remarks

The main result of this paper is formula (27) which gives the polarization dependence of an inter-configurational two-photon transition between Stark components arising from the configurations $n\ell$ and $n'\ell'$ of opposite parities. The obtained formula bears the same form as the corresponding one for intra-configurational two-photon transitions.

The intensity parameters I in (27) are, likewise in the case of intra-configurational two-photon transitions, model-dependent. More precisely, they depend on the wave-functions for the initial and final states and on the odd crystal-field parameters. They also incorporate the information coming from the involved symmetry group. They can be calculated in an *ab initio* way or may be considered as phenomenological parameters.

Finally, we would like to mention that the model developed in the present work applies to the case of $n\ell^N \rightarrow n\ell^{N-1}n'\ell'$ two-photon transitions with $\ell + \ell'$ odd. (The passage from one-electron configurations to N-electron configurations does not affect the symmetry considerations.)

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